



Electrochemical oxidation of several chlorophenols on diamond electrodes: Part II. Influence of waste characteristics and operating conditions

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Abstract

The electrochemical treatment of wastes containing several chlorophenols (4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol) using boron-doped diamond electrodes is described. Both direct and indirect processes are involved in the oxidation of the organics, indirect processes being mediated by oxidising agents (such as hypochlorite or peroxodisulphate) generated on the surface of the anode. The influence of the waste characteristics (initial concentration, pH and supporting media) is reported. The presence of reversible redox reagents, like the sulphate/peroxodisulphate redox couple, plays an important role in determining the global oxidation rate. Hypochlorite formation depends only on the organochlorinated compound and not on the presence of other reversible redox reagents in the waste. Alkaline pH favours the accumulation of carboxylic acid intermediates since, under these conditions, the oxidation rate of such compounds is low. The influence of the operating conditions (temperature and current density) is also discussed. The results show that high temperatures improve the rate of the mediated reactions and that high current density values decrease the efficiency of the direct electrochemical processes.

1. Introduction

The use of direct and mediated electrochemical oxidation for the treatment of aqueous wastes has undergone rapid development in recent years [1–5]. This technology can be successfully applied to the treatment of wastewater containing non-biodegradable organics such as phenol, chlorophenol or aniline [6–10].

The waste characteristics have a marked influence on the rate and efficiency of the electrochemical process because the organic compounds contained in the wastewater may have different degrees of oxidisability. Moreover, the pH of the waste greatly influences the current efficiency and, for aromatic compounds, the nature of reaction intermediates. In this sense, the supporting medium also significantly affects the treatment results, since it influences the nature of the mediated reagents electrogenerated at the anode surface [11, 12].

In addition to the waste characteristics, operating conditions play an important role in the electrochemical oxidation of organic wastewaters [13–16]. Two parameters are considered to affect the process: current density and temperature.

Temperature markedly influences mediated electrochemical processes, since high values favour the occurrence of chemical oxidation reactions. Therefore, an

increase in temperature will increase the oxidation reaction rate and the current efficiency.

Conversely, the current density markedly affects the reaction rate of direct and mediated electrochemical processes. The oxidation rate is diffusion-controlled only when direct electrochemical reactions occur and high current densities are employed [17]. An increase in the current density will therefore lead to the appearance of diffusion limitations and, consequently, to a lower efficient. This decrease in the process efficiency can be partially compensated if secondary reactions generate oxidising agents that are able to directly oxidise the organics. High current density values increase the formation of these electrogenerated compounds.

The electrochemical oxidation also depends on the type of anode employed. In addition to more traditional materials (DSA, SnO₂, PbO₂, etc.) [18–20], recent years have seen anodes based on diamond layers – the advantages of which include good chemical resistance and high efficiency [9, 11, 12, 21].

The goal of the present work was to increase understanding of the mechanisms involved in the electrochemical oxidation of chlorophenols on boron-doped diamond electrodes. A model for this system was proposed in Part I [22], which involved studying the influence of the waste characteristics (initial concentration, supporting

electrolyte and pH) and the operating conditions (current density and temperature). As in part I, the chlorophenols (CP) studied were 4-chlorophenol (MCP), 2,4-dichlorophenol (DCP) and 2,4,6-trichlorophenol (TCP) [22].

2. Experimental

2.1. Analytical procedures

Total organic carbon concentration was monitored using a Shimadzu TOC-5050 analyzer. COD was determined using a HACH DR200 analyzer. Carboxylic acids were monitored using a Supelcogel H column, with a mobile phase of 0.15% phosphoric acid solution at a flow rate of 0.15 ml min⁻¹. The UV detector was set at 210 nm. Aromatics were monitored using a Nucleosil C₁₈ column, with a mobile phase of 40% water/60% acetonitrile, at a flow rate of 0.50 ml min⁻¹. In this case the UV detector was set at 270 nm.

2.2. Determination of the instantaneous current efficiency (ICE)

The chemical oxygen demand method was used for the determination of the current efficiency for the oxidation of several chlorophenols. In this method, the COD was measured during electrolysis and the instantaneous current efficiency was calculated using the relation:

$$ICE = \frac{[\text{COD}_{t+\Delta t} - \text{COD}_t]FV}{8I\Delta t} \quad (1)$$

where COD_{*t*} and COD_{*t*+ Δt} are the chemical oxygen demand (in g O₂ dm⁻³) at times *t* and *t* + Δt (in seconds), respectively, *I* is the current intensity (A), *F* is the Faraday constant (96 487 C mol⁻¹), *V* is the volume of the electrolyte (dm³) and 8 is a dimensional factor for unit consistence (32 g O₂ · mol⁻¹ O₂)/(4 mol e⁻ · mol⁻¹ O₂).

2.3. Electrochemical cell

The oxidation of chlorophenols was carried out in a single-compartment electrochemical flow cell previously described [22]. Diamond-based materials (BDD) were used as the anode and stainless steel (AISI 304) as the cathode.

2.4. Experimental procedures

Galvanostatic electrolyses were carried out to determine the influence of the main parameters in the process. The average composition of the wastewater used in the experimental assays was 1.10 mmol dm⁻³ of chlorophenol (MCP, DCP and TCP), 5000 mg Na₂SO₄ dm⁻³ and H₂SO₄ in suitable amounts to give a pH of 2 (or NaOH to reach a pH of 12). The pH was kept constant at these values during electrolysis by the continuous introduction of sulphuric acid (or sodium hydroxide) to the electrolyte reservoir. In order to determine the influence of supporting media an experiment using Na₃PO₄/H₃PO₄ medium was carried out. Likewise, in some experiments the influence of current density and temperature was studied by increasing the values to 60 mA cm⁻² and 60 °C, respectively. The initial organic matter concentration was also increased in some assays, except for TCP due to its low solubility. Table 1 shows the conditions applied in each experimental run for every tested compound. The cell potential was constant during each electrolysis, indicating that neither appreciable deterioration of the electrode nor passivation phenomena took place. The electrolyte flow rate through the cell was 1250 ml min⁻¹.

3. Results and discussion

3.1. Influence of waste characteristics

The galvanostatic electrolysis of the three chlorophenols was compared under the same operation conditions

Table 1. Experimental conditions studied in this work

Expt. run	Compound	Co/mg dm ⁻³	pH	ρ /mA cm ⁻²	<i>T</i> /°C	Media
1	MCP	140	2	30	25	Na ₂ SO ₄
2	MCP	140	12	30	25	Na ₂ SO ₄
3	MCP	140	2	30	25	Na ₃ PO ₄
4	MCP	2000	2	30	25	Na ₂ SO ₄
5	MCP	2000	12	30	25	Na ₂ SO ₄
6	MCP	2000	2	60	25	Na ₂ SO ₄
7	MCP	2000	2	30	60	Na ₂ SO ₄
8	DCP	180	2	30	25	Na ₂ SO ₄
9	DCP	180	12	30	25	Na ₂ SO ₄
10	DCP	180	2	30	25	Na ₃ PO ₄
11	DCP	2000	2	30	25	Na ₂ SO ₄
12	DCP	2000	12	30	25	Na ₂ SO ₄
13	DCP	2000	2	60	25	Na ₂ SO ₄
14	DCP	2000	2	30	60	Na ₂ SO ₄
15	TCP	220	2	30	25	Na ₂ SO ₄
16	TCP	220	12	30	25	Na ₂ SO ₄
17	TCP	220	2	30	25	Na ₃ PO ₄

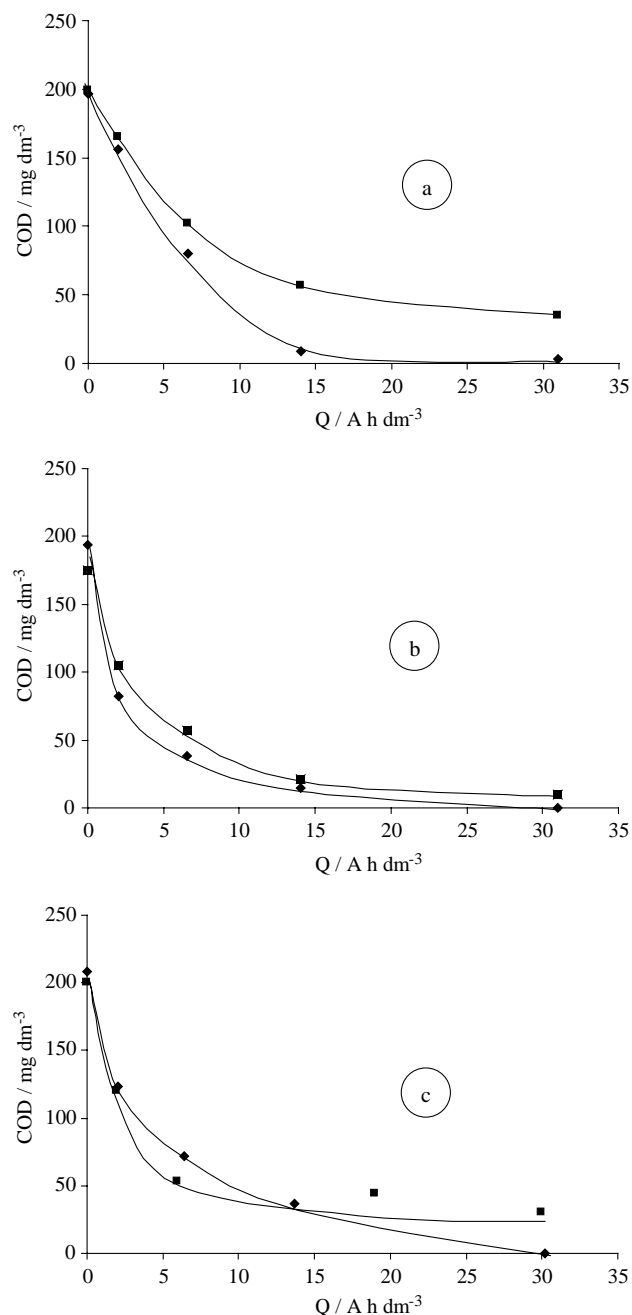


Fig. 1. Variation of COD with the specific electrical charge passed in the electrochemical oxidation of wastes containing CPs. Experimental conditions: C^0 : 1.1 mM, T : 25 °C, ρ : 30 mA cm⁻². (a) MCP: ◆ run 1; ■ run 3; (b) DCP: ◆ run 8; ■ run 10; (c) TCP: ◆ run 15; ■ run 17 (see Table 1).

($C^0 = 1.1$ mM; $T = 25$ °C; $\rho = 30$ mA cm⁻²; pH = 2) in supporting media containing sulphates or phosphates

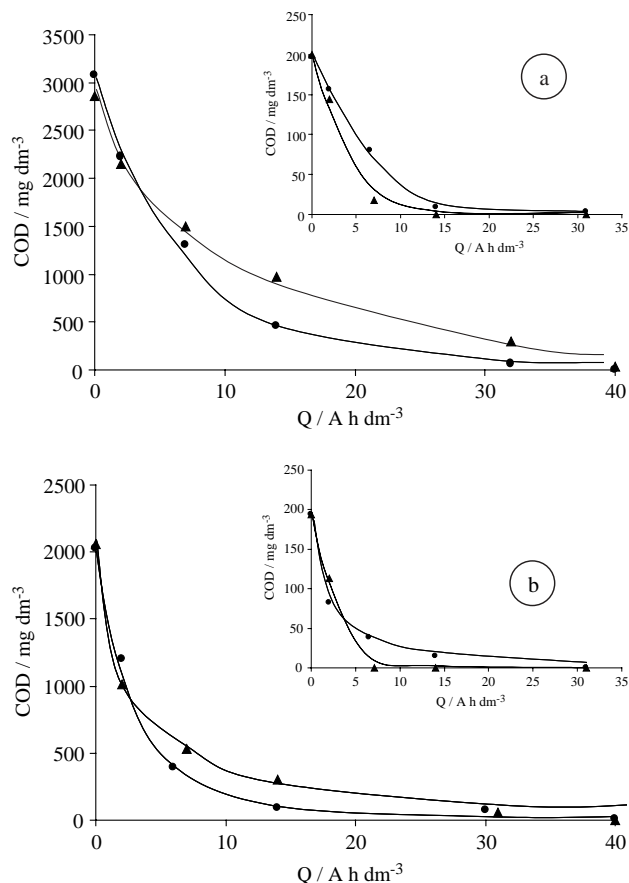


Fig. 2. Variation of COD with the specific electrical charge passed in the electrochemical oxidation of wastes containing CPs. Experimental conditions: T : 25 °C, ρ : 30 mA cm⁻². (a) MCP: ● runs 1 and 4; ▲ runs 2 and 5; (b) DCP: ● runs 8 and 11; ▲ runs 9 and 12 (see Table 1).

in water. The results of this study are represented in Figure 1.

The oxidation rate is higher in media containing sulphates than in media containing phosphates. Likewise it can be observed that the difference decreases with the chlorine content of the organic pollutant. The higher rate in sulphate media can be easily explained by taking into account [11, 12] that in such media some electro-generated reagents like peroxodisulphate can be formed, as discussed in Part I of this work. The smaller difference observed for the DCP and the TCP can be easily justified in terms of the formation of hypochlorite [8, 23] by means of the oxidation of the chloride ions released from the chlorophenols. Hypochlorite was detected in both systems (sulphate and phosphate media) in similar

Table 2. Maximum concentrations measured (mg dm⁻³) for the main intermediates detected in the galvanostatic electrolysis of solutions containing 1.1 mmol dm⁻³ of MCP, DCP and TCP

Intermediates	MCP		DCP		TCP	
	Na ₂ SO ₄	Na ₃ PO ₄	Na ₂ SO ₄	Na ₃ PO ₄	Na ₂ SO ₄	Na ₃ PO ₄
Oxalic acid	48.9	59.0	85.4	96.9	115.6	125.0
Maleic acid	3.3	3.4	3.5	4.1	1.4	1.6
Fumaric acid	0.9	1.1	1.0	1.3	1.2	1.5

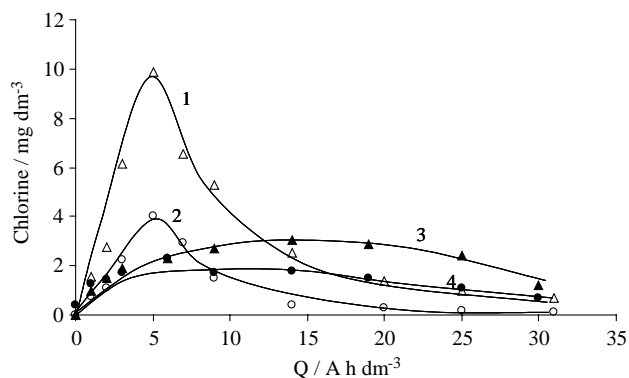


Fig. 3. Variation of chlorine fractions with the specific electrical charge passed in the electrochemical treatment of TCP (1.10 mM) at different pH. (1) Δ pH 12, hypochlorite; (2) \circ pH 12, chloride ion; (3) \blacktriangle pH 2, hypochlorite; (4) \bullet pH 2, chloride ion.

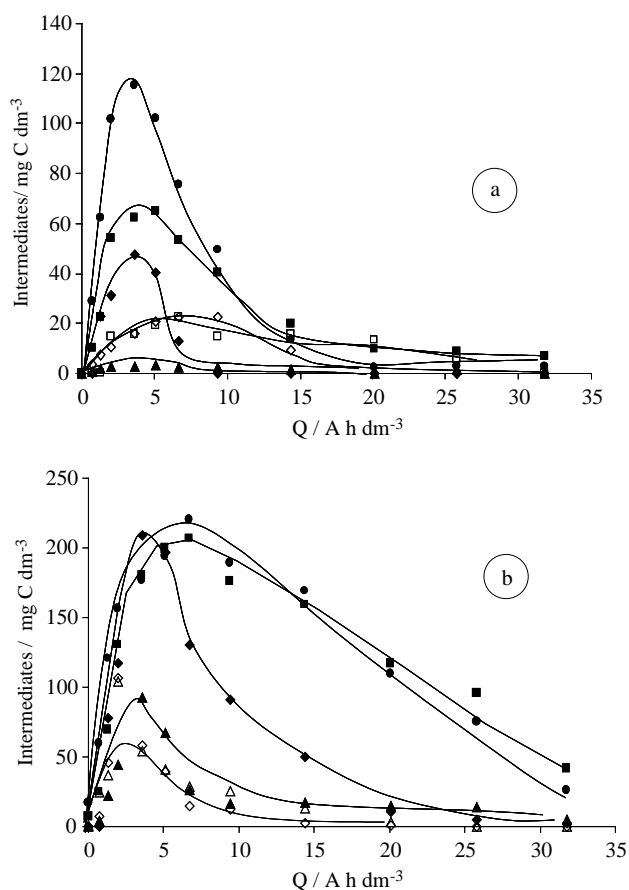


Fig. 4. Variation of 4-chlorophenol intermediates and products obtained with the specific electrical charge passed. Experimental conditions: C^0 : 2000 mg dm⁻³, T : 25 °C, ρ : 30 mA cm⁻²; \blacksquare oxalic acid; \bullet maleic acid; \blacktriangle fumaric acid; \blacklozenge formic acid; \diamond hydroquinone; \triangle benzoquinone and \square trichloroacetic acid. (a) pH 2; (b) pH 12.

concentrations, showing that its formation depends only on the organochlorinated compound and not on the presence of other redox reagents. The concentration of hypochlorite increases with the chlorine content in the organic pollutant and so it also increases the rate of the oxidation processes decreasing the differences in the reactions rates in both media.

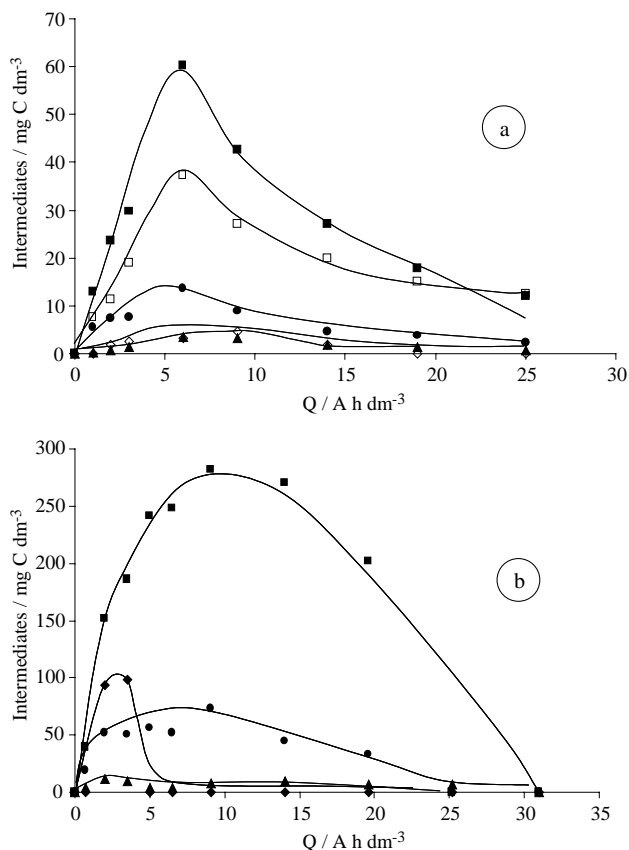


Fig. 5. Variation of 2,4-dichlorophenol intermediates and products obtained with the specific electrical charge passed. Experimental conditions: C^0 : 2000 mg dm⁻³, T : 25 °C, ρ : 30 mA cm⁻²; \blacksquare oxalic acid; \bullet maleic acid; \blacktriangle fumaric acid; \blacklozenge formic acid; \diamond hydroquinone and \square trichloroacetic acid. (a) pH 2; (b) pH 12.

Thus, the presence of reversible redox reagents (peroxodisulphate or others), which can be oxidised at the anode surface, and later act as intermediaries for shuttling electrons between the pollutant substrate and the electrode, plays an important role in the global oxidation rate. However, it can be observed (Table 2) that in both cases the same organic intermediates are formed and in similar concentrations, indicating that these redox reagents do not influence the process mechanisms.

Figure 2 shows the effect of the pH of the waste for different initial concentrations of MCP and DCP in supporting media containing sulphates. It is apparent that there are different trends for high and low concentrations. In both cases the initial oxidation rate is higher in alkaline media. However, as the galvanostatic electrolysis develops, the oxidation rate in acidic media surpasses those in the alkaline media.

The higher initial rate observed in all cases can be explained by the higher initial concentration of hypochlorite measured at this pH, as can be observed in Figure 3. Hypochlorite can act as a redox reagent and thus increases the global oxidation rate. The low concentration of chloride and hypochlorite measured at acidic pH can be explained [24] by taking into account that the haloform reaction is favoured under these

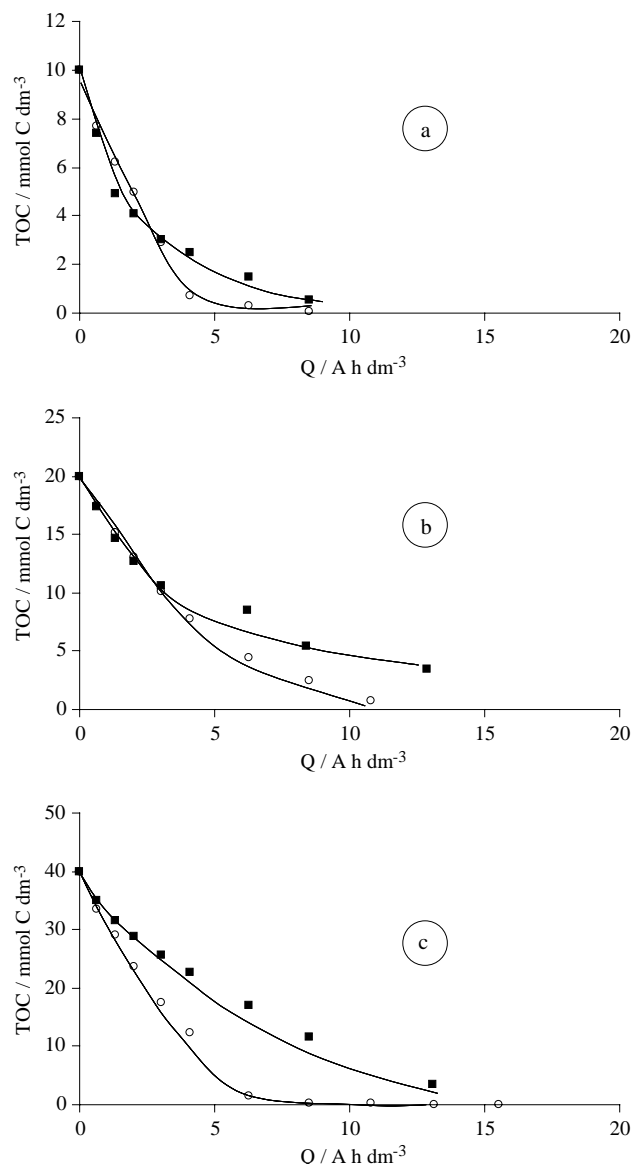


Fig. 6. Variation of TOC with the specific electrical charge passed in the electrochemical oxidation of wastes containing formic acid (a), oxalic acid (b) and maleic acid (c). Experimental conditions: C^0 : 10 mM, T : 25 °C, ρ : 30 mA cm⁻²; ○ pH 2, ■ pH 12.

conditions and, therefore, a larger amount of chlorine reacts with maleic acid to form volatile organochlorinated compounds.

The different behaviours observed at different pH values, can be understood in terms of the intermediates formed during the oxidation process. Figures 4 and 5 show the main intermediates formed in the electrolysis of the wastes with a high concentration of MCP and DCP, respectively. It can be seen that carboxylic acids (mainly maleic and oxalic) are the intermediates formed in the largest amounts and that the maximum concentration reached is higher at alkaline pH. This supports the idea that the oxidation rate is limited by the rate of the carboxylic acid oxidation step, which must be lower at alkaline pH.

In an attempt to confirm this lower oxidation rate of carboxylic acids at alkaline pH, a number of electrolysis

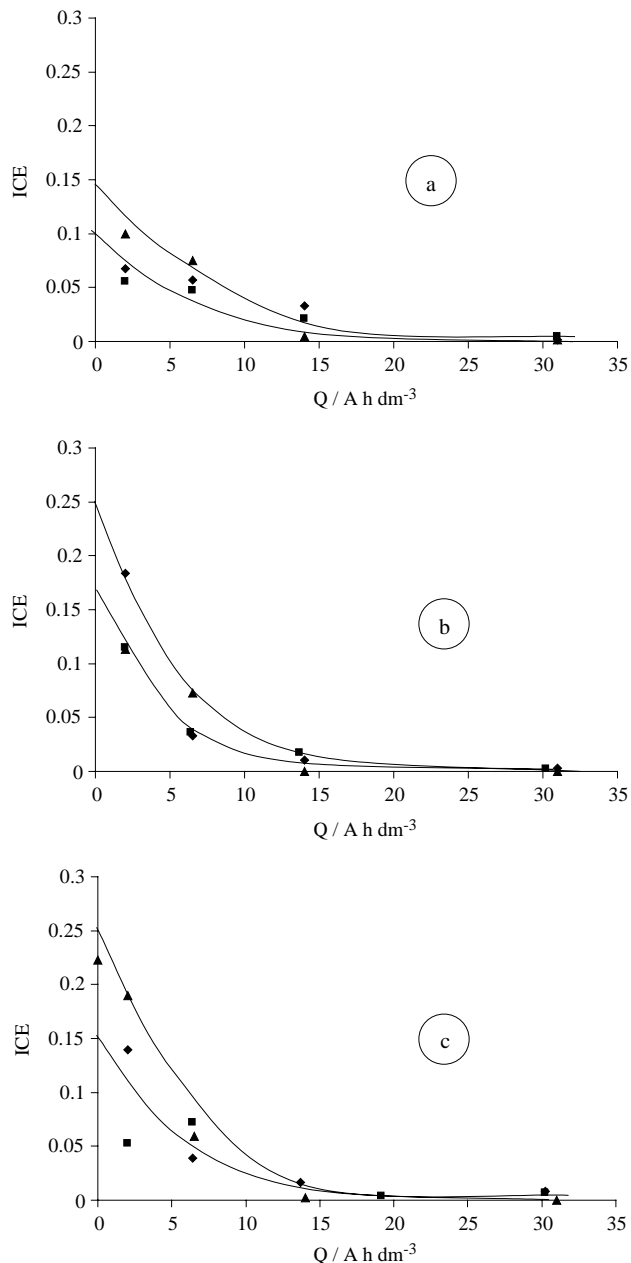


Fig. 7. Variation of the ICE with the specific electrical charge passed in the electrochemical oxidation of wastes containing CPs. Experimental conditions: C^0 : 1.1 mM, T : 25 °C, ρ : 30 mA cm⁻². (a) MCP: ◆ run 1; ▲ run 2; ■ run 3; (b) DCP: ◆ run 8; ▲ run 9; ■ run 10; (c) TCP: ◆ run 15; ▲ run 16; ■ run 17 (see Table 1).

assays were performed on wastes containing 10 mM formic, oxalic and maleic acids in water (5000 mg Na₂SO₄ dm⁻³). The same operation conditions were used in each assay (T = 25 °C; ρ = 30 mA cm⁻²) and only the pH of the supporting medium was modified. The results of these assays are represented in Figure 6. It can be observed that, for the carboxylic acids tested, the mineralisation rate is lower at pH 12, mainly for the maleic acid case. Thus, the larger amounts of aliphatic acids generated at alkaline pH are a result of the slower oxidation rate for these compounds.

In low-concentration chlorophenol wastes, the high electrical charge/organics concentration ratio minimises

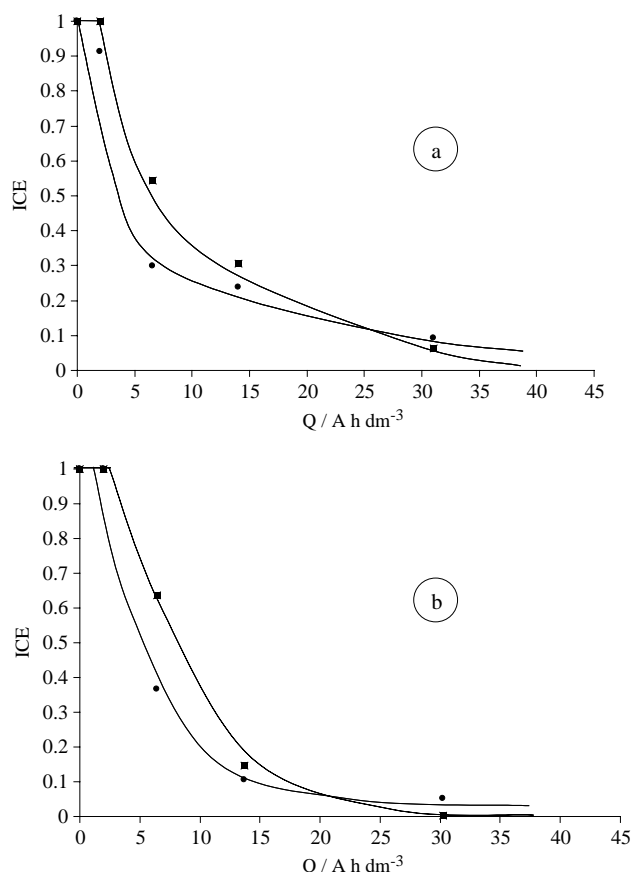


Fig. 8. Variation of the ICE with the specific electrical charge passed in the electrochemical oxidation of wastes containing CPs. Experimental conditions: T : 25 °C, ρ : 30 mA cm^{-2} . (a) MCP: ■ run 4; ● run 5; (b) DCP: ■ run 11; ● run 12 (see Table 1).

the amount of intermediates formed, and the global oxidation rate is therefore higher in alkaline media, since it is not limited by the carboxylic acid oxidation stage. Conversely, highly concentrated chlorophenol wastes, carboxylic acids are accumulated due to their low oxidisability in comparison with other intermediates and, as a result, the global oxidation rate is controlled by the carboxylic acid oxidation rate. Consequently, the global oxidation rate is higher in acidic conditions.

Figures 7 and 8 show the evolution of the ICE with specific electrical charge passed as a function of supporting electrolyte and pH for both low and high concentrations, respectively. Low concentrations cause the appearance of diffusion limitations and the ICE values are correspondingly low. When high concentrations are studied, ICE can achieve values near to 1 at the beginning of the electrolysis before decreasing with time to finally reach a value not far from zero.

Sulphate media give rise to higher ICE values than phosphate media. Conversely, the influence of the pH depends on the concentration range studied. At low initial concentrations alkaline media give better efficiency than acid media, and the behaviour is opposite with high initial concentrations. These results are consistent with those previously obtained during the study of the behaviour of the process [22].

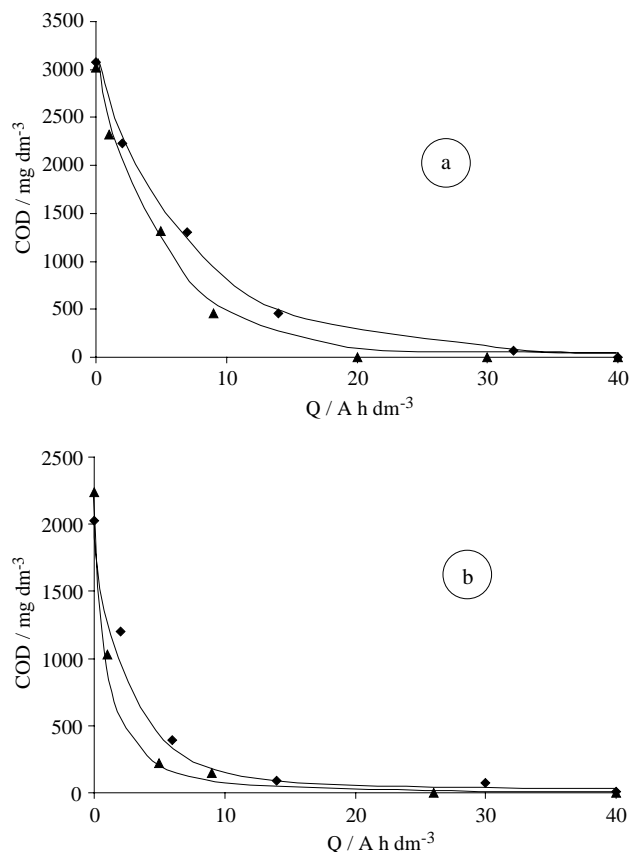


Fig. 9. Variation of COD with the specific electrical charge passed in the electrochemical oxidation of wastes containing CPs. Experimental conditions: C^0 : 2000 mg dm^{-3} , pH: 2, ρ : 30 mA cm^{-2} . (a) MCP: ◆ run 4; ▲ run 7; (b) DCP: ◆ run 11; ▲ run 14 (see Table 1).

3.2. Influence of operating conditions

Figure 9 shows the influence of temperature on the electrochemical oxidation of MCP and DCP aqueous wastes ($C^0 = 2000 \text{ mg dm}^{-3}$; 5000 $\text{mg Na}_2\text{SO}_4 \text{ dm}^{-3}$; pH = 2).

The global oxidation rate increases with temperature. Since direct oxidation processes remain almost unaffected by temperature, this fact must be explained in terms of the presence of inorganic electrogenerated reagents. The oxidation carried out by these redox reagents is a chemical reaction and, consequently, its rate normally increases with temperature. This fact confirms that the oxidation processes proposed [22] can be carried out either at the electrode surface and by electrogenerated reagents – mainly hypochlorite and peroxodisulphates. However, new organic intermediates are not formed with increasing temperature, indicating that the process mechanisms do not vary with temperature.

Figure 10 shows the influence of current density. Increase in current density leads to an increase in the oxidation rate but, at the same time, leads to a less efficient process since higher charges are required to remove the same amount of organic matter. This behaviour is characteristic of diffusion-controlled pro-

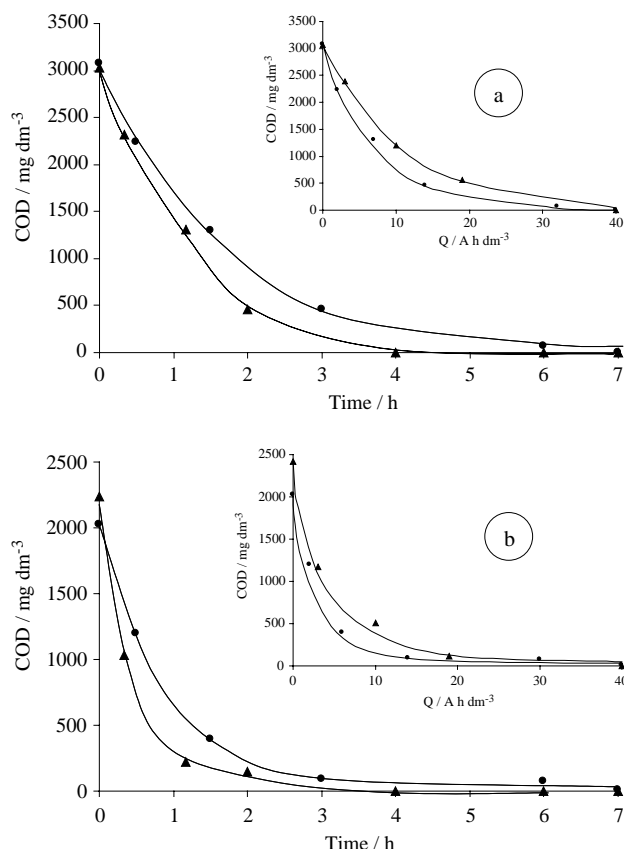


Fig. 10. Variation of COD with the time and the specific electrical charge passed in the electrochemical oxidation of wastes containing CPs. Experimental conditions: C^0 : 2000 mg dm^{-3} , pH: 2, T : 25°C . (a) MCP: ● run 4; ▲ run 6; (b) DCP: ● run 11; ▲ run 13 (see Table 1).

cesses. In such systems, an increase in current density cannot increase the rate of oxidation of the organics at the electrode and only favours the anodic side reactions. Since these reactions do not all generate oxidised redox reagents, a decrease in efficiency is observed. Therefore, both direct and mediated oxidation processes play an important role in the electrochemical oxidation of chlorophenols.

Figure 11 shows the ICE vs. specific electrical charge passed as a function of temperature and current density. The variation with temperature is similar to those obtained using the reference conditions and two zones can be distinguished: a kinetic-controlled zone with ICE values close to 1 and a diffusion-controlled zone with ICE values decreasing exponentially with Q . No significant differences can be observed. Conversely, increasing current density leads to a change in the ICE vs. Q dependence trend. A less pronounced variation is observed and this can be interpreted in terms of a more important role for electrogenerated redox reagents in the global oxidation process.

4. Conclusions

(1) Electrochemical technologies using boron-doped diamond electrodes can be used for treating wastes

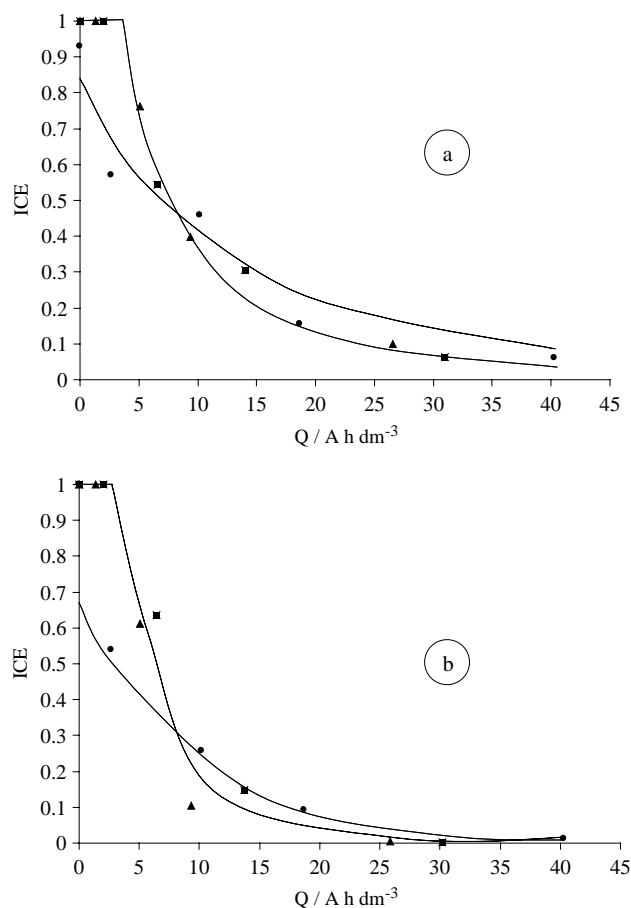


Fig. 11. Variation of the ICE with the specific electrical charge passed in the electrochemical oxidation of wastes containing CPs. Experimental conditions: C^0 : 2000 mg dm^{-3} , pH: 2. (a) MCP: ■ run 4; ● run 6; ▲ run 7; (b) DCP: ■ run 11; ● run 13; ▲ run 14 (see Table 1).

containing a range of chlorophenols. This treatment is able to remove almost completely the COD of the waste regardless of the operation conditions used.

(2) The results obtained agree with the mechanism proposed in Part I of this study [22] in which it was concluded that both direct and indirect processes are involved in the oxidation of the organics. The indirect processes are mediated by oxidising agents such as hypochlorite or peroxodisulphate, and these are generated on the surface of the anode.

(3) Waste characteristics have a marked influence on the development of the process. The presence of reversible redox reagents, like the sulphate/peroxodisulphate redox couple, plays an important role in the global oxidation rate. Hypochlorite formation depends only on the organochlorinated compound and not on the presence of other reversible redox reagents in the waste. Alkaline pH favours the accumulation of carboxylic acid intermediates, since under these conditions the oxidation rate of these compounds is low.

(4) High temperatures improve the mediated reactions and increase the global oxidation rate. The application of high current densities decreases the yield of the direct process because this causes an increase in the diffusion

limitations. However, higher current densities can also increase the formation of indirect reagents. As a consequence, the oxidation rate increases with current density applied, while the efficiency decreases.

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